Defense Technical Information Center
Compilation Part Notice

ADP012640

TITLE: Effects of Ion Bombarding and Nitrogenation on the Properties of Photovoltaic a-CNx Thin Films

DISTRIBUTION: Approved for public release, distribution unlimited

This paper is part of the following report:

TITLE: Progress in Semiconductor Materials for Optoelectronic Applications Symposium held in Boston, Massachusetts on November 26-29, 2001.

To order the complete compilation report, use: ADA405047

The component part is provided here to allow users access to individually authored sections of proceedings, annals, symposia, etc. However, the component should be considered within the context of the overall compilation report and not as a stand-alone technical report.

The following component part numbers comprise the compilation report:
ADP012585 thru ADP012685

Effects of Ion Bombarding and Nitrogenation on the Properties of Photovoltaic a-CN$_x$ Thin Films

Z.B. Zhou * , R.Q. Cui, G.M. Hadi, Q.J. Pang

Solar Energy Institute, Department of Physics, Shanghai Jiaotong University,
Shanghai 200030 China

C.Y. Jin, Z. M. Ding

Instrumental Analysis Center, Shanghai Jiaotong University,
Shanghai 200030 China

ABSTRACT

Amorphous carbon nitride films (a-CN$_x$) were synthesized by using single ion beam sputtering of a graphite target in argon and nitrogen sputtering gases. This thin film could be used as a novel photovoltaic material. The films were characterized with the technique of laser Raman, spectroscopic ellipsometry and electron spin resonance spectrometer (ESR). In this paper we report the effects of ion impacting and nitrogenation on the microstructure, density of defect states, bonding character, optical and photovoltaic properties. Effective decreasing of intensity of the ESR signal and formation of C-N bonding were observed, which could be attributed to the increment of the impinging ions on the growing films. The nitrogenation of a-CN$_x$ films could decrease the Tauc optical gap (0.62~0.86eV) and the intensity of ESR signal, increase photon absorption coefficient of the films (10^6~10^4cm^{-1}).

The primary photovoltaic values of the devices having Schottky structure of ITO/CN$_x$/Al are I$_{sc}$ 1.56 μ A/cm^2 and V$_{oc}$ 250 mV, respectively, when exposed to AM1.5 illumination (100mW/cm^2, 25℃).

INTRODUCTION

The interest in carbon nitride thin films was referred to the theoretical calculation of its possible crystal structure β –C$_3$N$_4$ in 1980s [1,2]. This crystalline alloy is claimed in the ranking of hardest materials. Since that time, many efforts have carried out to synthesis this new crystal material with less success [3]. Actually, the carbon nitride films with amorphous structure might be a rather promising novel electronic material considering its electrical, optical properties can be controlled by changing the concentration of nitrogen atoms in the thin films or by choosing different deposition processes [3,4]. This new material possesses some peculiar properties, such as negative electron affinity, low dielectric constant and high photoconductive gain, so it could be used on field emitting displays, interlayer of integration circuits and photovoltaic devices [5-7]. The synthesis of carbon nitride films can be achieved with variety techniques, such as plasma enhanced CVD [8,9], unbalanced magnetron sputtering [10], ion-beam deposition [11], laser ablation and FCVA [12,13]. In all of these processes, the ion bombardment during the deposition is one of the most important factors, which affects the bonding structure, electronic and optical properties of thin films. In this work, the films we studied were deposited by the method of single ion beam sputtering process (SIBS). We mainly studied the effects of ion bombardment and nitrogenation processing conditions on the properties of the

amorphous carbon nitride thin films for photovoltaic application. We adjusted the amount of the energetic ions bombarding on the films, and successfully controlled the bonding configuration and many other properties. Some protocol Schottky thin film solar cells with the structure of ITO/a-CN$_x$/Al were fabricated in order to investigate the photoactive property of the a-CN$_x$ thin film material.

EXPERIMENTAL DETAILS

The deposition equipment for a-CN$_x$ thin films is a set of single ion beam sputtering instrument with a Kaufman ion source. The synthesizing system also consists of a diffusion pump, water-cooled target holder and substrate holder. The background and operating pressure in the vacuum chamber are better than 1×10^{-4} Pa and 3×10^{-2} Pa, respectively. A high purity graphite target (99.95%) was used as sputtering target. Nitrogen with high purity (99.999%) was used for both sputtering ions to bombard the target and nitrogen species to incorporate with carbon ions in the films. Nitrogen gas was ionized and extracted by powerful electrical field produced by accelerating grid electrode. An energetic ion beam was formed, which provided both sputtering ions and reacting nitrogen precursors. The energy and current intensity of the ions coming from the ion beam source were 740eV and 65mA/cm^2. The substrate holder, with an ion beam impact angle of about 80 degrees, between ion beam and normal line of substrate surface, consisted of a water-cooled copper plate, which kept substrates at ambient temperature during the deposition. We use two kinds of substrates: quartz sheets coated with ITO for Schottky solar cell processing and polished silicon wafers for characterization of a-CN$_x$ thin film.

The structure of carbon nitride thin film solar cells ITO/a-CN$_x$/Al was described elsewhere [14,15]. A number of Schottky solar cells having this structure were produced based on a set of depositing conditions. We found that only a portion of these solar cells showed a testable photovoltaic performance. We tried to obtain the correlation between the process condition and their photoexcited character below.

MEASUREMENT AND DISCUSSION

In order to recognize this new material, we use some modern probes including laser Raman, ESR and spectral ellipsometry for characterization.

Spectral ellipsometry test

Table I .Deposition condition and test results for three typical samples.

	A	B	C
Incident angle θ (degree)	75	85	75
N/(N+Ar) pressure rate	0.5	0.5	1
D$_r$ (nm)	5.67	0.11	5.43
D$_{a\text{-}CN_x}$ (nm)	100.7	135.9	120.1
Tauc`s optical band gap (eV)	0.86	0.74	0.62

In variable angle spectral ellipsometry (VASE) measurement, we can change the polarization of light as a function of angle and wavelength when light is reflected from or transmitted through a sample. The samples used for spectral ellipsometry test were

prepared on silicon substrates. The optical model for the test is composed of three layers, the first one is the surface roughness whose thickness D_r is about several nanometers, the second is a-CN_x layer described by the Lorentz model and the third is the SiO_2 substrate whose thickness is supposed to be infinite. The experimental results (including the concentration of nitrogen gas in the sputtering gases and ion impact angle θ) for three typical samples are listed in table I .The substrates would receive more bombarding ions under the condition of smaller ion impact angle θ . So the films we get have a larger thickness of roughness layer.

The spectra for the complex refractive index as a function of optical wavelength for the three typical a-CN_x films (A, B, C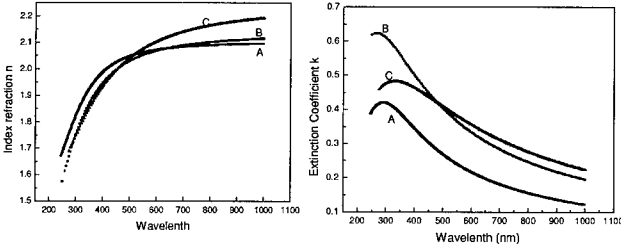) are shown in figure 1.(a) (b). The curves exhibit a smooth behavior, which is the characteristic of amorphous semiconductor[16]. The values of n (E) and k (E) are in the ranges 1.6~2.2 and

Figure 1. Spectra of the complex refractive index of the a-CN_x films for three typical depositing conditions (a) Refractive index n vs. wavelength (b) Extinction coefficient k vs. wavelength

0.1~0.6, respectively. In the short wavelength region, for small impact angle θ , we observed higher values of n and lower values of k, as in Fig.1(a, b). The sample (A) shows lower extinction coefficient than the samples (B) and (C). This can be attributed to a relative low concentration of nitrogen in the sputtering gases and a smaller incident angle of the ion beam, which correlates with a trend toward better diamond-like properties. A higher concentration of nitrogen in the sputtering gases corresponds to a higher k as shown in Fig. 1(b).
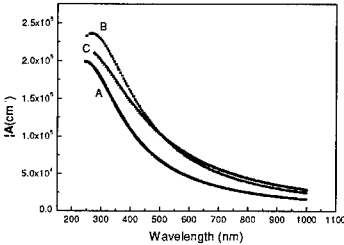

Figure 2 shows the variation of optical absorption coefficient α as a function of the optical wavelength, which was obtained from ellipsometry test results. We find that the absorption coefficient in the region 500nm ~1100nm is about $1 \times 10^5 \sim 2 \times 10^4 cm^{-1}$, which is higher than that of a-Si:H thin films and arises from transitions between localized states.

Figure 2. Variation of optical absorption with photon wavelength

We obtain the optical gap E_0 defined by the formula (1) from the curves of the $E \times \varepsilon_2^{1/2}$ versus photon energy E , shown in Fig.3. Deviations of the data from linearity at low energies arise from transitions in exponential band tails below the absorption edge and are characteristic of amorphous semiconductors.

$$\omega^2 \varepsilon_2(\omega) = B(\hbar\omega - E_0)^2 \tag{1}$$

By extrapolating the liner parts to the energy axis, the values so obtained are in the range $0.62 \sim 0.86 eV$, which depends on the different depositing conditions. Sample A, deposited with a lower nitrogen concentration in working gases and lower ion impact angle, possesses a higher optical gap $0.86 eV$. Sample C, with a high concentration of nitrogen in working gas, shows a relatively smaller optical gap $0.62 eV$.
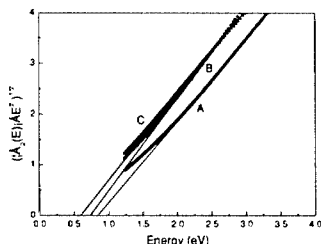

Figure 3. Tauc-plots for determining the optical band gap of three samples A, B, C

Raman test

Raman spectroscopy is a non-destructive method for measuring the bonding structure of materials. Usually, the sp^2 contribution is always dominant in a Raman spectrum because the sp^2 bonding is more sensitive to visible laser light. Therefore, the Raman spectra are dominated by G peak at about 1580 cm^{-1} and D peak around about 1350 cm^{-1}. A.C. Ferrari and J. Robertson once made a full interpretation of Raman spectra for amorphous and graphic carbon films [17]. In our work, Raman spectra of our carbon nitride films were obtained using Dilor Raman spectrometer (Ne-He laser, excitation wavelength 633 nm). Spectra were recorded from wavenumbers 800cm^{-1} to 1800 cm^{-1} shown in Fig. 4. The 950 cm^{-1} peak arises from the silicon substrate [18].
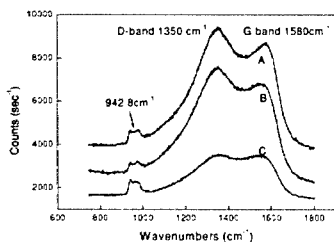

Figure 4. Raman spectra of amorphous carbon nitride thin films, D-band and G-band are located at about 1350 cm^{-1} and 1580 cm^{-1}, respectively

The conclusion of peak fitting with gaussian functions explicitly shows three peaks situated at the centers of about 1370 cm^{-1}, 1570 cm^{-1} and 1240cm^{-1}, as seen in Fig.5 (deconvoluted spectra of sample A and B are not given here). The first two are definitely contributed from D-band (disordered band) and G-band (graphite band), respectively, which is the same as the previous research report on amorphous carbon. Here, the 1240cm^{-1} peaks are designated the N band for the origin of 1240cm^{-1} peak is postulated to be due to C-N stretching bonding as reference [19] mentioned.

The C=N peak in the Ref. [18] should located at ~1450 cm^{-1} which was not recognized in our deconvoluted spectra. The position of N band peak was considered to shift to lower wave numbers in our sample C. The relative intensity of D and G peaks (I_D/I_G) can be taken to indicate relative sp^3/sp^2 ratio indirectly, also the relative intensity of N and G peaks (I_N/I_G) was supposed to show the nitrogen relative concentration in the films qualitatively. The conclusion was listed in table II.
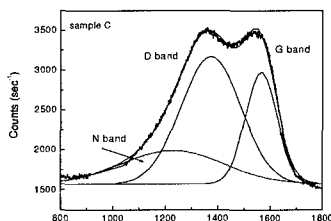
Figure 5. Deconvoluted spectra of sample C

The tendency of variation of the G position with the amount of bombarding ions received by substrates was coincident with the results discussed in reference [16]. Comparing sample A with C and B, we could get that the nitrogenation and ion bombarding initiate a red shift of the G band position. A higher rate of I_D/I_G corresponds to a lower ratio of sp^3/sp^2, which was reported in the paper [16] and many other literatures [18]. The function of ion striking the

thin film surface is to remove weak and unstable bonds. As the ion bombarding, CN trip-bond is removed easily, C≡N is partially removed and C-N is preserved. This result is consistent with the known stability of the bond structure of carbon and nitrogen [20]. It also lowers the rate of I_D/I_G, however, nitrogenation can promote the rate of I_D/I_G. Therefore, the sp^3/sp^2 ratio of the sample A is higher than that of the other two. The relative nitrogen concentration in the film C is

Table II.Deposition condition and Raman test results for three typical samples.

	A	B	C
Incident angle θ (degree)	75	85	75
N/(N+Ar) pressure rate	0.5	0.5	1
G band (cm⁻¹)	1575	1568	1566
D band (cm⁻¹)	1370	1371	1374
N band (cm⁻¹)	1251	1261	1228
I_D/I_G	1.04	1.06	1.10
I_N/I_G	0.66	0.60	0.69
PV performance of Schottky solar cells	Poor	Poor	Good

highest among the three samples. Its atomic percentage of nitrogen is 16 % tested by XPS techniques in the Ref.[15], which have been shown in our previous work [15].

The sample C has another apparent difference compared with A and B. It has much lower N band position 1228cm⁻¹, while that of sample A and B are 1251 cm⁻¹ and 1261 cm⁻¹.

Electron Spin Resonance spectra and photovoltaic property
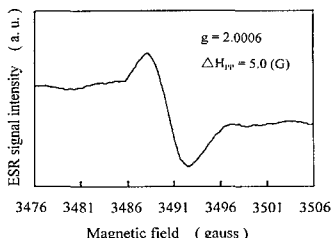

Figure 6. Electronic spin resonance spectrum of a-CN$_x$ sample C. Sample A and B has much more intensive ESR signal than sample C

In order to compare unpaired electron densities of different samples, we measure the ESR spectra by using a conventional Bruker electron spin resonance spectrometer (ER200D-ESR X-band, Modulator frequency 100kHz). ESR measurements were made at room temperature. The g values obtained from the ESR spectra of all samples were found to be about 2.0006 and peak-to-peak width was found to lie in a wide range 5~12G as shown in Fig. 6. Sample C had a lowest relative electron spin density and a trongest photovoltaic signal among all samples. Ion bombarding and nitrogenation have a diminution function, or passivation effect, to the defect states, which

usually exist in amorphous materials. The Schottky junction made from sample C exhibited open circuit voltage 250mV and short circuit current 1.56 μ A/cm^2.

CONCLUSION

Ion impacting to the films and nitrogenation during deposition play key roles on the properties of photovoltaic application orientated amorphous carbon nitride films. They could effectively decrease electron spin resonance density, promote the photo-activity. They could increase the C-N bonding which could be accountable for the photoactive character of the films. Ion impinging can increase optical band gap, decrease photon absorption while nitrogenation has an opposite effect. How to retain their advantages and diminish their negative function to meet the photovoltaic requirement is a task for the future work.

REFERENCES

1. Y. Liu and M. L. Chen, Science **245**, 841 (1989)
2. B.C. Yang, et al, Chinese Physics Lett. **16**, 847 (1999)
3. L.K. Cheah, X. Shi, et al, Materials Science and Engineering **B64**, 6-11 (1999)
4. Deuk Yeon Lee, Yong Hwan Kim, et al, Thin Solid Films **355-356**, 239-245 (1999)
5. A. Grill, Diamond and Related Materials **10**, 234-239 (2001)
6. T. Iwasaki, et al, Diamond and Related Materials **8**, 440 (1999)
7. M. Maldei, D.C. Ingram, Solar Energy materials and Solar Cells, **51**, 433-440 (1998)
8. S.F. Durrant, E.C. Rangel, et al, J. Vac. Sci. Technol. **A 13**, 361 (1995)
9. J.H. Kim, D.H. Ahn, et al, J. Appl. Phys. **82**, 658 (1997)
10. N. Savvides, J. Appl. Phys. **59**, 4133 (1986)
11. B. Enders, Y. Horino, et al, Phys. Rev. **B121** 73(1997)
12. Z.-M. Ren, Y.-C. Du, et al, Appl. Phys. Lett.**65** 1361(1994)
13. E. Liu, X.Shi, Surface and Coatings Technology **120-121** 601-606 (1999)
14. Z.B. Zhou, R.Q. Cui Applied Surface Science **172** 245-252 (2001)
15. Z.B. Zhou, R.Q. Cui and G.M. Hadi, Solar Energy Materials and Solar Cells **70** 487-493(2002)
16. M.H. Brodsky, Amorphous Semiconductor, New York (Springer-Verlag 1979) p73-109
17. A.C. Ferrari and J. Robertson, Physical Review B **61(20)**, 14095-14107 (2000)
18. M. Neuhaeuser, H. Hilgers, et al, Diamond and Related Materials **9**, 1500-1505 (2000)
19. J.H. Kaufmann, S. Metin, D.D. Saperstein, Phys. Rev. B **39 (18)**, 13053 (1989)
20. A.K.M.S. Chowdhury, D.C. Cameron, et al, Thin Solid Films, **332**, 62-68 (1998)